

Sub7FT:

Business & Industry?, File 9 (1994 - present)

ABI/INFORM?, File 15 (1971 - present)

Gale Group PROMT?, File 16 (1990 - present)

Gale Group PROMT?, File 160 (1972-1989)

Gale Group Trade & Industry Database?, File 148 (1976 - present)

Gale Group Computer Database?, File 275 (full-text 1/1988 - present)

Business Wire, File 610 (Mar 1999 - present)

Business Wire, File 810 (1986 - February 1999)

Dialog Global Reporter, File 20 (May 1997 - present)

The McGraw-Hill Companies Publications Online, File 624 (1985 - present)

Gale Group New Product Announcements/Plus? (NPA/Plus, File 621 (1985 - present)

Gale Group Newsletter Database?, File 636 (1988 - present)

PR Newswire, File 613 (May 1999 - present)

San Jose Mercury News, File 634 (Jun 1985 - present)

PR Newswire, File 813 (May 1987 - May 1999)

Set#	Query
L1	((identif\$7 or report\$3) and qualit\$3 and repair and work and perform\$3 and generat\$3 and facilit\$3 and estimat\$3 and (sort\$3 or filter\$3))
L2	((identif\$7 or report\$3) and qualit\$3 and repair and work and perform\$3 and generat\$3 and facilit\$3 and estimat\$3 and (sort\$3 or filter\$3))

3/9/25 (Item 25 from file: 15)

02614650 ? ? ? ? ? 356967071

Occupational exposure to diesel exhaust in the canadian federal jurisdiction

**Seshagiri, Baily; Burton, Steven**

**AIHA Journal ? v64n3 ?pp: 338**

**May/Jun 2003**

**ISSN: 1529-8663 ?Journal Code: AIH**

**Document Type: Periodical; Feature ?Language: English ?Record Type: Fulltext**

**Special Feature: Table Graph**

**Word Count: 5838**

**Abstract:**

To assess the impact of the proposed American Conference of Governmental Industrial Hygienists threshold limit value-time-weighted average to diesel particulate matter (DPM), 177 full-shift samples were taken in 23 workplaces under Canadian federal jurisdiction. National Institute for Occupational Safety and Health (NIOSH) Method 5040 (Elemental Carbon: Diesel Exhaust) was used to assess exposure. **Quality** control tests were conducted prior to field sampling by taking air samples in the exhaust stream of two diesel engines mounted on a test bed and having them analyzed by two laboratories using the same thermal program. Field sampling results indicated that 77% of the elemental carbon (EC) levels were below the currently proposed limit of 20  $\mu\text{g}/\text{m}^3$ , and 54% below 10  $\mu\text{g}/\text{m}^3$ . The geometric mean concentration of EC was 24.4  $\mu\text{g}/\text{m}^3$  in high-activity and 4.0  $\mu\text{g}/\text{m}^3$  in low-activity **work** sites. Corresponding arithmetic mean concentrations were 41.4 and 8.4  $\mu\text{g}/\text{m}^3$ , respectively. The ratio of EC to total carbon (TC) was close to 90% for all **quality** control samples. It was no higher than 50% for the field samples, and it varied significantly with EC concentration. Finally, results are presented from the analysis of 41 samples by a third laboratory using a thermal-optical method slightly different from NIOSH 5040. Even if one were to opt for EC as a surrogate for DPM, unless analysis details (particularly the thermal program) are specified, significant differences in the results can be expected. This could lead to problems for regulatory agencies and for epidemiologic research. [PUBLICATION ABSTRACT]

?

**Text:**

To assess the impact of the proposed American Conference of Governmental Industrial Hygienists threshold limit value-time-weighted average to diesel particulate matter (DPM), 177 full-shift samples were taken in 23 workplaces under Canadian federal jurisdiction. National Institute for Occupational Safety and Health (NIOSH) Method 5040 (Elemental Carbon: Diesel Exhaust) was used to assess exposure. **Quality** control tests were conducted prior to field sampling by taking air samples in the exhaust stream of two diesel engines mounted on a test bed and having them analyzed by two laboratories using the same thermal program. Field sampling results indicated that 77% of the elemental carbon (EC) levels were below the currently proposed limit of 20  $\mu\text{g}/\text{m}$

$\text{sup } 3$

, and 54% below 10  $\mu\text{g}/\text{m}$

$\text{sup } 3$

. The geometric mean concentration of EC was 24.4  $\mu\text{g}/\text{m}$

$\text{sup } 3$

in high-activity and 4.0  $\mu\text{g}/\text{m}$

$\text{sup } 3$

in low-activity **work** sites. Corresponding arithmetic mean concentrations were 41.4 and 8.4  $\mu\text{g}/\text{m}$

sup 3

, respectively. The ratio of EC to total carbon (TC) was close to 90% for all **quality** control samples. It was no higher than 50% for the field samples, and it varied significantly with EC concentration. Finally, results are presented from the analysis of 41 samples by a third laboratory using a thermal-optical method slightly different from NIOSH 5040. Even if one were to opt for EC as a surrogate for DPM, unless analysis details (particularly the thermal program) are specified, significant differences in the results can be expected. This could lead to problems for regulatory agencies and for epidemiologic research.

Keywords: diesel exhaust, diesel particulate, elemental carbon, thermal-optical method, TLV(R)

In 1995 the American Conference of Governmental Industrial Hygienists (ACGIH) served notice(1) that it intended to classify diesel particulate matter (DPM) as a Category A2 carcinogen and assign it a threshold limit value-time-weighted average (TLV(R)-TWA) of 0.15 mg/m

sup 3

. It amended this notice in 2001 and lowered the proposed TLV-TWA to 0.02 mg/m

sup 3

(as elemental carbon [EC]) while retaining the A2 carcinogen classification.(2) In 1983 NIOSH **estimated** that approximately 1.35 million workers in the United States were occupationally exposed to the combustion products of diesel fuel in about 80,000 workplaces. In Canada roughly 100,000 to 130,000 workers are similarly exposed in a variety of sectors such as railways; highway transport; telephone and telegraph systems; pipelines; canals; ferries; tunnels and bridges; shipping and shipping services; radio and television broadcasting and cable systems; and airports. Because the ACGIH TLVs are commonly used to evaluate occupational exposure to hazardous contaminants, a national project was undertaken by the Canadian federal government to assess the impact of the proposed TLV for DPM. The results of that project are presented here. A number of excellent reviews of the health effects of diesel emissions have been published(3-5) recently and are not discussed here.

The primary objective of the project was to quantify exposure to DPM using EC as a marker. However, when the project was initiated in 1997, it was apparent that the analytical procedures for measurement of DPM were not very common. NIOSH method 5040 Elemental Carbon (Diesel Exhaust)

sup (6)

had just been published, and there were very few commercial laboratories that could analyze for EC using this method. In fact, in Canada there was only one laboratory that had recently acquired the necessary instrumentation to **perform** this analysis. Hence, it was decided to conduct some **quality** control tests to validate the procedures used by this laboratory.

TABLE I. Regression Analysis of Results of Validation Tests

METHODS AND MATERIALS

**Quality** Control Tests

Forty-five air samples were collected on preweighted, 37-mm, quartz fiber **filters** mounted in open-faced cassettes, placed directly in the diluted exhaust of two diesel engines mounted on a dynamometer in an engineering laboratory operated by the Canada Centre for Mineral and Energy Technology (CANMET) in Ottawa, Ontario. One engine was a Deutz BF6M1013CP. It was run at 2000 rpm, 75% of full load (495 lb-ft). The second engine was a Mercedes OM62. That engine was operated at full load at about 1400 rpm. The temperature at the exhaust manifold was approximately 520[degrees]C. The exhaust was diluted with ambient air prior to sampling. The exhaust temperature at the sampling location was 12[degrees]C. Eight samples were taken at a time. The sampling manifold was located horizontally along the center line of the exhaust duct and was connected to a constant flow pump operating at a nominal flow rate of 20 L/min. Duration of sampling was varied from 10 to 30 min. Two blanks were collected for each set of samples. Efforts were made to obtain **filter** loadings equivalent to airborne concentrations of about 0.5 mg/m

sup 3

to 0.03 mg/m

sup 3

, that is, from about three times to one-fifth of the TEV of 0.15 mg/m

sup 3

initially proposed by ACGIH in 1995. Human Resource Development Canada's (HRDC) Industrial Hygiene Laboratory in Ottawa carried out the gravimetric analysis of the **filters** before sending them to the first laboratory (Lab 1) for EC analysis. They used a portion of the **filter** for analysis and sent a portion to another laboratory (Lab 2). Laboratories 1 and 2 participated in the interlaboratory round-robin test of analysis of carbonaceous aerosols organized by NIOSH.

#### Results of **Quality** Control Tests

EC loadings ranged from about 3 to 50 [mu]g/cm

sup 2

. Both laboratories **reported** EC as well as total carbon (TC) detected on the **filters**. Regression analysis was carried out to compare the results from the two laboratories. Table I shows the results of the analysis. The correlation coefficient, *r*, between the EC loadings **reported** by the two laboratories was 0.99. The slope of the regression line was 0.98. The correlation coefficient between the EC and TC loadings **reported** by each of the laboratories was 1, and the slope of the regression line was 0.9 for Lab 1 and 0.92 for Lab 2. The slightly lower value of the slope is a reflection of the fact that TC is made up of organic carbon (OC) and carbonate carbon (if present) as well as EC. The correlation coefficient between EC **reported** by the two laboratories and total dust (TD) was 0.99. The slope of the regression line was 0.84 for Lab 1 and 0.87 for Lab 2, indicating that the total dust contains other unidentified particulate matter in addition to TC. Finally, the table shows the regression of the ratio of EC to TC **reported** by the two laboratories with EC. The correlation coefficient in each case is quite low; but more to the point, the slope of the regression line is close to zero. This is an indication that the regression line is nearly horizontal. The intercept of the regression line was 87.9 for Lab 1 and 94.4 for Lab 2. This shows that for pure diesel exhaust taken under strict laboratory conditions the ratio EC to TC is very high, well into the 90%

range, and that the ratio is independent of the EC loading.  
Field Measurements

#### Work Site Descriptions

In 23 **work** sites grouped into five categories, 177 full-shift air samples, both area and personal, were taken. Each **work** site was subjectively classified into either a low-, medium-, or high-activity site.

#### Bus **Repair** Garages

The bus **repair** garages (six sites, 50 samples) were large operations with up to 20 bays. All of them had local exhaust ventilation in addition to general dilution ventilation. They had areas for parking buses indoors and **facilities** for washing and cleaning the buses. There was a considerable amount of bus movement within the garages. Two of the garages were classified subjectively as high-activity **work** sites and four as medium-activity **work** sites.

#### Truck **Repair** Garages

The truck **repair** garages (seven sites, 40 samples), on the other hand, were relatively small, with no more than two to six bays. Truck movement within the garages was extremely limited, and the motors were operated infrequently, in some instances only a few times a day, to allow the trucks to enter and exit. The trucks were in these garages mainly for mechanical repairs. In a few garages local ventilation was provided by means of exhaust pipe hookups. In general, mechanical ventilation was poor. Two of these garages were classified as medium-activity sites and five as low-activity sites.

#### Locomotive Workshops

The locomotive workshops (4 sites, 40 samples) were very large **facilities**, some of them with canopy-type ventilation in addition to dilution ventilation. However, the locomotives were rarely operated inside the workshops. They were pushed in and pulled out by mechanical means. All four sites were classified as low-activity.

#### Tunnels

The road tunnel, open 24 hours a day, 365 days a year, went under a major river and had two lanes of traffic, one in each direction. It was about 1.6 km long from portal to portal, with a 6.7 m-wide road bed. Mechanical exhaust ventilation, with make-up air units, appeared to be functioning well. The traffic was a mixture of trucks, buses, and automobiles. Sixteen samples were taken on two separate occasions. On the first occasion a diesel-powered heavy-duty truck was being used to operate a diesel-powered vacuum unit to clean the debris from under the road bed. This caused a huge increase in diesel emissions. This operation is conducted only a couple of times a year. To assess the exposure under more routine conditions, air samples were taken on another day during which the cleaning operation was not being conducted.

TABLE II. Descriptive Statistics of EC Concentrations at Different Activity Levels

The airport service road (nine samples), which separated the main terminal building from the baggage handling area and the tarmac, was virtually a tunnel. The road was about a kilometer long, 10 m wide, and ran under the terminal building; that is, except for the two ends of the road, it was

totally enclosed with doors leading to the main terminal building on one side and to the baggage handling area and the tarmac on the other. The ceiling height was about 5 m. The road was heavily used by cars, delivery trucks, garbage trucks, service vehicles for the airlines, and so on. A significant number of vehicles using this road were diesel powered. Ventilation was provided along the length of the road, but did not appear to be very effective (although ventilation was subsequently improved, sampling was not repeated). There were no workers permanently stationed along this road, but the employees who drove the diesel-powered tractors that carry luggage were exposed to DPM. The road tunnel was classified as a high-activity **work** site, and the service road as a medium-activity **work** site.

#### Others

Nine air samples were taken in the diesel equipment maintenance workshop of a wharf. It was a small **facility** with virtually no movement of vehicles within the building during the day, except when the doors were opened to allow the vehicles to enter and depart. Mechanical ventilation was not provided. Occasionally, the motors were run up for adjustment, which could have resulted in a significant accumulation of diesel emissions. This was classified as a low-activity **work** site.

Seven air samples were taken in the administrative and passenger service areas of a large urban bus terminal. The service areas were housed in a building that led to the actual loading platforms. These areas were provided with their own mechanical ventilation systems. Diesel emissions could enter these areas through the doors leading to the loading platforms. The loading platforms themselves were open to the outside and provided with separate mechanical ventilation. This was classified as a low-activity **work** site. A personal sample was taken on a baggage handler who spent most of his time in the loading area, and this was classified as a medium-activity **work** site. Six samples were taken in the cabs of armored trucks while they were in operation. These were classified as low activity.

TABLE III. Descriptive Statistics of EC Concentrations for Different **Work** Site Groups

#### Measurement Details

Samples were taken to measure the concentrations of DPM, nitric oxide, nitrogen dioxide, and carbon monoxide. Only the results of the DPM measurements are presented in this article.

As per NIOSH Method 5040, air samples to quantify DPM were collected on preweighed, 37-mm, quartz fiber **filters** mounted in open-face cassettes, at a nominal flow rate of 2 L/min. The **filters** were analyzed gravimetrically for TD loading at HRDC's Industrial Hygiene Laboratory. They were then sent to Lab 1 for EC analysis using the same parameter files that had been established for the QC samples. The detection limit for this method is about 2 [mu]g/**filter**.

Seventy-nine personal and 98 area samples were taken to measure the concentrations of DPM. The sampling duration was generally of the order of 7 to 8 hours. Results **reported** have not been normalized to an 8-hour time duration. The vast majority of samples were taken in areas where there were sources of diesel emissions. However, a few samples were taken in adjacent areas such as parts storage areas and supervisory offices.

#### RESULTS AND DISCUSSION

##### Statistical Description of EC Concentration

A probability plot of the log transform of the EC concentration was used to confirm that measured EC concentration was log-normally distributed, as one would expect from industrial hygiene samples. Tables II-IV show the statistical descriptors of EC concentration. These include the following: number of samples; arithmetic mean; geometric mean; standard deviation; geometric standard deviation; median; and maximum. All concentrations are expressed in micrograms per meter cubed ([mu]g/m

sup 3

). As mentioned previously, the **work** sites sampled were subjectively classified into low-, medium-, or high-activity levels. Table II shows the breakdown of the statistics for each of these categories. Table III shows the breakdown of the statistics according to the **work** site groupings previously described (bus **repair** garages, truck **repair** garages, locomotive workshops, tunnels, and others). Finally, the EC concentration statistics for personal and area samples are shown in Table IV. The difference in the mean values between the low- and high-activity **work** sites and between the medium- and high-activity **work** sites was statistically significant at the 95% level. The maximum EC concentration was 217.5 [mu]g/m

sup 3

, which was measured in the road tunnel during roadbed cleaning.

TABLE IV. Descriptive Statistics of EC Concentrations for Personal and Area Samples

The EC concentration in 77% of all samples was less than the currently proposed TLV of 20 [mu]g/m

sup 3

. Four percent of the samples were greater than 100 [mu]g/m

sup 3

; 5% between 50 and 100; 15% between 20 and 50; 23% between 10 and 20; 16% between 5 and 10; and finally, 38% were less than 5 [mu]g/m

sup 3

. Visual representation of the above statistics are shown in Figures 1-3, known as "box plots." They characterize the distribution of a variable, displaying its median, the 25th percentile, the 75th percentile, and values that are far removed from the rest, also called outliers. Figure 1 shows the box plot of the EC concentration for all samples. The line inside the box represents the median, in this case about 9 [mu]g/m

sup 3

. The lower boundary of the box is the 25th percentile, which is about 3 [mu]g/m

sup 3

. In other words, 75% of all samples exceed this concentration. The upper boundary of the box represents the 75th percentile, which was about 19 [mu]g/m

sup 3

. The length of the box corresponds to the interquartile range, which is the difference between the 75th and 25th percentiles. Box plots for the three activity levels, as well as for the five **work** site groups are shown in Figures 2 and 3, respectively. The box plot includes two categories of cases with outlying values. Cases with values that are more than three box-lengths from the upper or lower edge of the box are called "extremes" and are **identified** with a solid downward-pointing triangle ([black triangle down]). Cases with values that are between 1.5 and 3 box-lengths from the upper or lower edge of the box are called "outliers" and are designated with a solid circle ([white circle]). The largest and smallest observed values that are not outliers are shown as the horizontal lines (also known as "whiskers") below and above the box. The box plots of all measurements are much more robust than the ones for specific categories, simply because of the greater number of samples in the former.

FIGURE 1. Box plot of EC concentration: all samples

The mean EC, TC, and TD concentrations for the three activity levels are shown in Table V. It is seen that although the EC concentration increases progressively from 8.4 to 41.4 [ $\mu$ g/m

sup 3

as activity level goes up, neither TC nor TD follow the trend. Both TC and TD concentrations are significantly higher for the medium activity level than for the low or high activity level. TD concentration at the low activity level is greater than at the high activity level. Correlation between EC and TC was found to be 0.318 (sig. 0.000); between EC and TD it was 0.141 (sig. 0.061); and between TC and TD, 0.458 (sig. 0.000). These results are not unexpected, because in most workplaces, if not all, sources of airborne particulate matter are not confined to diesel engines. These measurements also show that some of the particulate matter contribute to the TC burden. This would indicate that, at least for the types of workplaces surveyed, EC appears to be a better marker for diesel particulate matter than either TC or TD.

#### Verification of EC Results

All the methods currently available to quantify EC in diesel exhaust suffer from one major drawback: there is no standard for DPM to which the methods can be calibrated.(7) These methods have been called "operational" methods for that reason, in the sense that the methods themselves define the analyte. Although agreement between the methods is very good when it comes to the analysis of TC in a sample of DPM, it is far less impressive when it comes to EC. The reason appears to lie in the ability of the various methods to differentiate between OC and EC. The analysis method has a direct bearing in determining where this "split" occurs. In addition, the ability to correct for pyrolytically **generated** carbon is also an important factor in the quantification of EC. Lack of such a correction could lead to an overestimation of EC.

FIGURE 2. Box plot of EC concentration: different activity levels

FIGURE 3. Box plot of EC concentration: different **work** site groups

In the first set of round-robin tests (1995) identical samples of pure diesel exhaust were analyzed by 13 laboratories in Europe.(8) The conclusion was that "intercomparison of results on pure diesel engine



emissions is, in most cases, satisfactory, especially for EC and TC."(8, p. 171) However, it was noted that in another round-robin study among 12 laboratories conducted in the United States the results were very good for TC, but not so good for EC. The problem was attributed to the pyrolysis of OC, which is then **reported** as EC, as well as to the differences in the temperature profiles used by the various laboratories.

Eileen Birch of NIOSH conducted an interlaboratory comparison study in which 11 laboratories participated.(9) Six laboratories used NIOSH 5040 for their analysis. The pretreatment and thermal programs were identical. The NIOSH method corrects for pyrolytically **generated** char by transmitting a laser beam through the **filter** (thermo-optical transmittance, or TOT). One laboratory used a very similar method, with two differences.(10) First, the thermal program was not the same as that used by the other six laboratories. Second, instead of using **filter** transmittance to determine the EC-OC split, they used **filter** reflectance (thermo-optical reflectance, or TOR).

TABLE VI. Comparison of EC and TC Analysis by Different Techniques

TABLE V. Mean EC, TC, and TD Concentrations at Different Activity Levels

Four laboratories used a different thermal technique. The evolution of OC was achieved in a nitrogen atmosphere instead of helium. Their thermal program was significantly different from that used by the TOT and TOR laboratories. No correction was applied for char produced by pyrolysis. Thermally evolved carbon was oxidized to carbon dioxide and determined by coulometric titration. In the TOT and TOR procedures evolved carbon is catalytically oxidized to carbon dioxide, which is reduced to methane and quantified by a flame ionization detector (FID). According to reference 9, for the coulometric analysis "all samples are acidified before analysis to remove carbonates, which interfere in the coulometric determination of EC."(9, p. 853) The TOT and the TOR methods do not have any pretreatment for elimination of carbonates. The first phase of the pyrolysis procedure is expected to remove organic carbon as well as carbonate carbon. If any carbonates are present their contribution is added to that from OC and the total is **reported**.

The results of the NIOSH study are shown in Table VI. The minimum, maximum, and mean quantities of TC and EC per square centimeter of **filter** detected by the TOT, TOR, and coulometric methods are shown for samples taken in three different types of environments: urban, truck, and fire. The urban sample was taken at a construction site near a downtown area, the truck sample in a loading dock area where diesel trucks were being used, and the fire sample in the bay of a fire engine house. It is seen that the variability in the **reporting** of TC mean values between the TOT and the coulometric methods is acceptable, being on the order of 3 to 7% (of the TOT mean) for the different types of samples. However, when it comes to the **reporting** of EC, the variability ranges from 344% for the urban sample to 111% for the truck sample. The variability between the TOT mean and the TOR values were not as extreme, being 67% for the urban sample, 28% for the truck sample, and 23% for the fire. This is not surprising in light of the fact that both are thermo-optical methods that provide for correction of pyrolytic char. The primary difference lies in their respective thermal programs. The highest variability occurs at the lower **filter** loadings. The within-method variability for the results from only the TOT laboratories is about + or -10%. In terms of airborne concentration, the urban sample works out to about one-tenth of the proposed TLV, the truck sample to about one-third, and the fire sample to about seven-eighths, as per the results of the TOT analysis.

FIGURE 4. Verification tests, TC: Lab 1 versus Lab 3

In light of this apparent disparity among the results of the different analytical procedures, 30 samples and 11 blanks from the present measurements were sent to a third laboratory (Lab 3) for analysis using the TOR method. The results are shown in Figures 4 and 5. Figure 4 shows the plot of TC in micrograms per **filter** detected by the two laboratories (Lab 1 and Lab 3). The correlation coefficient was 0.98. The slope of the regression line was 1.03. Figure 5 shows the plot of EC detected by the two laboratories. Although the correlation is good (R

sub sq

= 0.91), there is still a considerable amount of scatter, particularly at the lower **filter** loadings. More important, there is a positive bias in the Lab 3 results; that is, it overestimates the amount of EC on the **filter** as compared to Lab 1. The equation of the regression line is

$$\text{Lab 3 EC} = 1.285 \times \text{Lab 1 EC} [\mu\text{g}/\text{filter}]$$

The difference is very close to that **reported** in reference 9 between TOT and TOR results, particularly for the truck and fire samples.

FIGURE 5. Verification tests, EC: Lab 1 versus Lab 3

The arithmetic mean values for all samples analyzed by both laboratories are shown in Table VI. It is seen that the difference between the TC values **reported** is very small (3.6% of Lab 1 mean). It is not statistically significant at the 95% level. However, the difference of 53.7% between the EC values is significant at the 99.5% level (paired samples t-test). Clearly, pinpointing the EC/OC split is method dependent and, more specifically, dependent on the thermal program being used. As mentioned previously, the TOR method is based on the sample reflectance to establish the OC/EC split time. This method seems to be quite discerning when it comes to organic nondiesel sources such as wood smoke, sucrose, and EDTA. However, in some of the field samples taken during the present project, a significant proportion of the deposits was black pyrolyzed carbon (PC) from diesel sources. The thermal program of the TOR method does not provide for separation of this type of PC, and it is included in the laboratory **report** as total EC. In such situations the TOR method tends to overreport the amount of EC present in the sample.

The TOT method uses an optical correction based on sample transmittance to establish the OC/EC split time. In addition, the temperature program used by the TOT method is more sophisticated compared with the TOR method. The sample is heated to 850[degrees]C in a helium atmosphere and allowed to cool to 650[degrees]C before 2% oxygen is introduced into the sample chamber. This allows any PC present to react first, producing a distinct signal peak approximately 360 sec from the beginning of the thermal program. The sample chamber temperature is then ramped in steps from 650 to 940[degrees]C. About 60 to 70 sec later any EC that might be present on the **filter** begins to evolve and produces a characteristic FID signal. This characteristic signal is seen clearly in the thermograms of the **quality** control samples starting after about 420 sec and with the peak occurring at about 520 sec. The EC peak of the thermogram is skimmed off the background signal from the FID. The background signal is the PC resulting either from pyrolysis of OC during the first phase of the analysis procedure, or from the sources of diesel emissions. The loading of some of the field sample **filters** with this black PC made it difficult for the laser to find the proper OC/EC split time even with the TOT method. However, the split time can be manually overridden by the operator if, when the thermogram is examined, it is evident that the split

time produced by the laser transmittance technique is incorrect. This was done during the present analysis. This point is also made by Epstein, Rentschler, and Birch, (11) who noted that without a manual adjustment the potential for error increases for certain types of samples.

The difference between the EC results obtained from the TOT and TOR methods is probably due to the amount of PC deposited on some of the field sample **filters**. When a diesel engine is not under load, the engine block pressure is reduced, and this results in a higher proportion of PC to EC being exhausted. The **quality** control samples were prepared using a diesel engine warmed up to operating temperature under a constant load. Hence, the QC samples had a high EC-to-PC ratio. Comparable EC results would be expected using either the TOT or the TOR method. The optical correction strategies of TOT and TOR methods appear to have been created to deal with outside environmental **filter** loadings and not those found in some workplaces. When the field samples were analyzed by the TOT method, the amount of PC collected on some of the **filters** made any meaningful optical correction for PC difficult. The ideal solution would be to examine the thermogram manually to ensure that a proper split time has been used, but this may be impracticable in the real world. The next best solution might be to use a split time determined by an analysis of prepared samples, such as the **quality** control samples used in the present investigation. Automatic determination of split time is likely to be useful only when **filters** with high initial transmittance are being analyzed.

FIGURE 6. Plot of EC concentration versus EC/TC percentage

The two procedures are examined in detail in references 9 and 10 in an attempt to **identify** the probable causes of the differences in their results.

#### Ratio of EC to TC

The ratio of EC to TC is a very important variable. All the methods discussed in the previous section are in reasonable agreement in quantifying TC, which is made up of EC and OC. However, there are significant differences in the results when it comes to EC. The primary reason is the lack of a calibration standard for diesel particulate emissions, which in turn renders the task of differentiating between OC and EC in a sample dependent on the analysis protocol. The so-called split between EC and OC is method dependent. If the ratio of EC to TC were to be constant, as is the case with pure diesel exhaust, it would be easier to more accurately quantify EC. Unfortunately, this is not the case, as seen in Figure 6, where EC/TC percentage is shown plotted versus EC concentration. The ratio appears to increase with increasing EC concentration, leveling off at about 50%. Data published in references 12-14 are also plotted on the same figure for comparison. Zaebst et al. (12) **reported** measurements of exposure of trucking industry workers to diesel exhaust. Their cohort included dock workers, truck drivers, and mechanics. Their measurements predated the publication of NIOSH 5040, but their EC analysis was based on the thermo-optical method used by NIOSH. Whittaker et al. (13) assessed the exposure of employees in the electric utility industry (linemen and winch truck operators) to diesel exhaust. They used the NIOSH method for quantifying EC concentrations. Groves and Cain (14) conducted a large-scale study in the United Kingdom to obtain quantitative information on workplace exposure to diesel engine exhaust. They used the coulometric method and their workplace groupings included (1) ambulance depots, (2) roll-on-roll-off (ro-ro) ferries, (3) railway **repair** shops and stations, (4) bus garages and **repair** shops, (5) vehicle testing **facilities**, (6) fork-lift truck operations, and (7) toll booths, set-down areas, and tunnel

**repair** sites.

The trend shown by all the measurements is very similar: a rapid increase in the ratio of EC/TC up to an EC concentration of about 25 [mu]g/m

sup 3

and a gradual leveling off beyond that. The variability in the EC to TC ratio is primarily related to the operating conditions of the engine and possibly its mechanical condition, as well as the presence of other sources of OC and EC. The particulate matter emitted by properly tuned engines when fully warmed up and under load is made up almost entirely of EC. This is borne out by the results of the **quality** control tests. On the other hand, engines that have just started up and are under low load emit particulate matter heavily contaminated with organic volatiles, including unburned fuel and possibly lubricating oils. Groves and Cain(14) noted that during their tests one particular engine when idling at low revs produced particulate matter with an EC-to-TC ratio of only 30%, which went up to as much as 80% when the engine was operating under load.

#### CONCLUSIONS

To quantify exposure to DPM, 177 full-shift air samples were taken in 23 different **work** sites. In addition, **quality** control tests prior to field sampling and verification tests after field sampling were carried out. The measurements showed a progressive increase in EC concentration from **work** sites where there was low activity in terms of diesel engine operation to those where the activity was higher. Neither TC nor TD followed this trend. For the types of workplaces surveyed during this project, EC appears to be a better marker for DPM than either TC or TD.

The EC concentration of about 77% of the samples was less than the currently proposed TLV of 20 [mu]g/m

sup 3

, 54% less than 10 [mu]g/m

sup 3

, and 91% less than 50 [mu]g/m

sup 3

. Most workplaces of the type surveyed should not have great difficulty in meeting the proposed TLV provided they have adequate mechanical ventilation.

The ratio of EC to TC in pure diesel exhaust is nearly 90% and is virtually constant. However, in field samples the ratio rarely exceeds 50% and varies significantly.

Significant variation in EC determination was observed between methods based on thermo-optical analysis (TOT and TOR), most likely due to the differences in the thermal programs. This could be of concern when enforcing exposure limits based on EC unless a specific method is prescribed.

#### ACKNOWLEDGMENTS

Dr. Eileen Birch of NIOSH was responsible for the analysis of the **quality** control samples in Laboratory 2. Her assistance is

gratefully acknowledged. Thanks to Dr. Mahe Gangal of CANMET for his assistance in taking the **quality** control samples. The support and encouragement given by Albert Pighin, director, Technical Services Unit, throughout this project is acknowledged with thanks. Finally, the cooperation of the employers and employees at the various **work** sites and the assistance of the regional staff of the Labour Program of HRDC was much appreciated.

#### REFERENCES

1. American Conference of Governmental Industrial Hygienists (ACGIH): Threshold Limit Values for Chemical Substances and, Physical Agents. Cincinnati, Ohio: ACGIH, 1995.
2. American Conference of Governmental Industrial Hygienists (ACGIH): Threshold Limit Values for Chemical Substances and Physical Agents. Cincinnati, Ohio: ACGIH, 2001.
3. California Environmental Protection Agency: Part B: Health Risk Assessment for Diesel Exhaust. Sacramento, Calif.: Office of Environmental Health Hazard Assessment, Air Toxicology and Epidemiology Section, 1998.
4. Health Effects Institute: Diesel Exhaust: A Critical Analysis of Emissions, Exposure and Health Effects. A Special **Report** of the Institute's Diesel Working Group. Cambridge, Mass.: Health Effects Institute, 1995.
5. U.S. Environmental Protection Agency (EPA): "Health Assessment Document for Diesel Exhaust" (EPA /600/8-90/057E; SAB review draft). Washington, D.C.: EPA, 2000.
6. National Institute for Occupational Safety and Health (NIOSH): NIOSH Manual of Analytical Methods, 4th ed., vols. 1-3 (DHHS Pub. no. 94-113). Cincinnati, Ohio: NIOSH, 1996.
7. Birch, M.E., and R.A. Cary: Elemental carbon-based method for occupational monitoring of particulate diesel exhaust: Methodology and exposure issues. *Analyst* 727:183-1190 (1996).
8. Guillemin, M., H. Cachier, C. Chini, et al.: International round robin tests on the measurement of carbon in diesel exhaust particulates. *Int. Arch. Occup. Environ. Health* 70:161-172 (1997).
9. Birch, M.E.: Analysis of carbonaceous aerosols: Interlaboratory comparison. *Analyst* 723:851-857 (1998).
10. Chow, J.C., J.G. Watson, L.C. Pritchett, et al.: The DRI thermal/optical reflectance carbon analysis system: description, evaluation and applications in U.S. air **quality** studies. *Atm. Environ.* 27A:1185-1201 (1993).
11. Epstein, P.S., M. Rentschler, and M.E. Birch: Experiences with NIOSH 5040: A rugged method for measuring occupational exposure to diesel particulate matter. Paper presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 1999, Orlando, Fla.
12. Zaebst, D.D., D.E. Clapp, L.M. Blade, et al.: Quantitative determination of trucking industry workers' exposure to diesel exhaust particulates. *Am. Ind. Hyg. Assoc. J.* 52:529-541 (1991).
13. Whittaker, L.S., D.L. MacIntosh, P.L. Williams: Employee exposure to diesel exhaust in the electric utility industry. *Am. Ind. Hyg. Assoc. J.* 60:635-640 (1999).

14. Groves, J., and J.R. Cain: A survey of exposure to diesel engine exhaust emissions in the workplace. Ann. Occup. Hyg. 44:435-447 (2000).

AUTHORS

Baily Seshagiri (a,b)

Steven Burton (a)

aTechnical Services Unit, Occupational Safety and Health and Fire Prevention Division, Labour Branch, Human Resources Development Canada (HRDC), Ottawa, Ontario, Canada K1A 0J2;

bRetired; present address: 115 Riverdale Avenue, Ottawa, Ontario, Canada, K1S 1R1

**THIS IS THE FULL-TEXT.**

Copyright American Industrial Hygiene Association May/Jun 2003

**Geographic Names: Canada**

**Descriptors: Studies; Occupational safety; Diesel fuels; Quality control**

**Classification Codes: 9130 (CN=Experimental/Theoretical); 9172 (CN=Canada); 5340 (CN=Safety management)**

**Print Media ID: 20167**

---